

Europäisch s Patentamt European Patent Office Office europ en des brevets



(11) EP 0 299 561 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:10.01.1996 Bulletin 1996/02

(51) Int Cl.6: C11D 3/50, C11D 3/39

(21) Application number: 88201376.6

(22) Date of filing: 01.07.1988

(54) Perfume and bleach compositions

Parfüm und Bleichmittel enthaltende Zusammensetzungen Compositions contenant un parfum et des agents de blanchiment

- (84) Designated Contracting States: CH DE ES FR GB IT LI NL SE
- (30) Priority: 09.07.1987 GB 8716219
- (43) Date of publication of application: 18.01.1989 Bulletin 1989/03
- (73) Proprietors:
 - UNILEVER N.V. NL-3013 AL Rotterdam (NL)
 Designated Contracting States:
 CH DE ES FR IT LI NL SE
 - UNILEVER PLC London EC4P 4BQ (GB)
 Designated Contracting States: GB
- (72) Inventors:
 - Sims, Peter Stanford Chester, Cheshlre CH3 5UX (GB)

- Carter, Peter
 Burton, Wirral, Merseyside L64 5TL (GB)
- (74) Representative: Bryant, Tracey et al Bedford MK44 1LQ (GB)
- (56) References cited:

- DERWENT JAPANESE PATENTS REPORT, vol. 86, no. 04, Section Ch. D, page 13; & JP-A-60 245 699
- Parfümerie und Kosmetik, vol. 61, no. 8, 1980, pages 285-289; B. Streschnak: "Probleme bei der Parfümierung von Waschpulvern"

Remarks

The file contains technical information submitted after the application was filed and not included in this specification

P 0 299 561 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).



Description

5

15

30

35

45

50

55

FIELD OF THE INVENTION:

The invention relates to perfume compositions which are stable to a commercially usable level in the presence of bleaching compositions comprising organic peracid bleaching materials. The invention also relates to bleaching compositions containing such perfumes. These bleaching compositions are particularly, but not exclusively, suited to the bleaching of fabrics, and for this purpose they may also contain detergent active compounds.

10 BACKGROUND TO THE INVENTION:

There has long existed a problem in the formulation of bleaching compositions in that the effective perfuming of such compositions is difficult to achieve. The perfume is required to remain stable at a commercially usable level during storage prior to use and then be available for effective delivery to the surface without being altered or destroyed by the bleach component.

Perfume is added to a bleach composition, in particular a detergent composition, to provide an olfactory benefit in the product during use and to enhance the olfactory properties of the treated surface.

The effective perfuming of fabric, as an example of surfaces, that has already been bleached and washed can be achieved by incorporation of a suitable perfume in a fabric conditioner to be added during the rinsing or drying stage subsequent to a bleaching and washing step, but this necessitates the introduction of an additional step in the laundry process.

The use of peracids in detergent formulations presents a particularly hostile environment for perfume compositions. The present invention provides organic peracid bleach-stable perfume compositions. It is also known to generate a peracid bleaching species in the wash liquor by incorporating a peroxide bleach material, for example sodium perborate, and a bleach precursor, for example N, N,N¹, N¹-tetraacetyl ethylene diamine (TAED). The present invention does not relate to these systems in which the peracid bleach species is formed in situ.

US-A-4289641 discloses deodorant detergent products comprising a scap, detergent adjuncts including a detergency builder (other than soap) and/or a bleach such as an organic peroxyacid, and a deodorant composition. The deodorant composition comprises a special combination of a plurality of deodorant active components selected from several different defined classes.

JP-A-60 245699 discloses a bleaching detergent composition comprising at least one perfume agent, monopersulphate bleach, zeolite and surfactant.

EP-A-0214789 discloses a dry, diperacid-based bleach product, which may comprise a fragrance component stabilised by isolation from the bleaching composition.

EP-A-0147191 discloses a bleach-stable deodorant perfume comprising perfume components which are judged to be stable in the presence of sodium perborate tetrahydrate and TAED bleach activator.

EP-A-0005618 discloses deodorant products other than for use on human skin, comprising a deodorant composition and a carrier therefor chosen from abrasive cleaners, bleaching agents, waxes, film-forming polymers or mixtures there-of. The deodorant composition comprises a special combination of a plurality of deodorant active components selected from several different defined classes, as in US-A-4289641 mentioned above.

GENERAL DESCRIPTION OF THE INVENTION:

In its widest aspect, the invention provides a bleach composition comprising an organic peracid bleach and a pertume composition comprising perfume components which do not contain alkenyl or alkynyl groups and have a PSV (as defined hereafter) of at least 65%, selected from the following classes:

- i) saturated alcohols
- ii) saturated esters
- iii) saturated aromatic ketones
- iv) saturated lactones
- v) saturated nitriles
- vi) saturated ethers
- vii) saturated acetals
- viii) saturated phenois
- ix) saturated hydrocarbons, and
- x) saturated aromatic nitromusks

the said perfume components constituting from 0.05 to 1% by weight of the bleach composition.

The terms "saturated" is used herein to define groups not containing alkenyl or alkynyl bonds.

In a more specific aspect, the invention provides a bleach composition as defined above comprising an effective amount of the organic peracid bleach and up to 10% by weight of the defined peracid-stable perfume composition.

Preferably, the peracid-stable perfume compositions for use in the present invention will contain at least 80%, preferably 90% by weight, of the components defined above. Preferably, the components listed will have PSV's of at least

The bleach composition may also contain detergent active materials and will be referred to as bleach and/or detergent composition in the further description of this invention. The term organic peracid bleach, as used herein, includes the organic peroxyacids and their salts, which are well described in the literature as having the ability of effective bleaching at lower wash temperatures of about 20°-60°C.

The organic peroxy acids usable in the present invention are compounds having the general formula:

wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an anylene group containing from 6 to 8 carbon atoms, n is 0 or 1, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example :

wherein M is H or a water-soluble, salt-forming cation. Where n = 0, they are sometimes also referred to as peroxycarboxylic acids and where n = 1, they belong to the class of per(oxy)carbonic acids.

Preferred organic peroxyacids are solid at room temperature up to about 40°C. They can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted

wherein Y can be H, -CH₃, -CH₂Cl,

40

5

10

15

20

25

30

35

and n can be an integer from 1 to 20, preferably from 4-16. 45

Examples of peroxyacids are peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids, particularly 1,12-diperoxydodecanedioic acid being preferred. Other examples of suitable aliphatic peroxyacids are diperoxyazelaic acid, diperoxyadipic acid, diperoxysebacic acid and alkyl(C₁-C₂₀) dipersuccinic acids.

When the organic peroxyacid is aromatic, the unsubstituted,acid may have the general formula:

wherein Y is, for example, hydrogen, halogen, alkyl,

55

The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid; diperoxyterephthalic acid; 4-chlorodiperoxyphthalic acid; diperoxyisophthalic acid; peroxy benzoic acids and ring-substituted peroxy benzoic acids, such as m-chloroperbenzoic acid and peroxy-alpha-naphthoic acid; and also magnesium monoperphthalate (obtainable under the tradename "H48" from Interox Chemicals Ltd).

Further examples of organic peroxyacid bleach compounds are described in the following patent literature: EP-A-0083560; EP-A-0105689; EP-A-0083560; EP-A-0166571; EP-A-0168204; EP-A-0195570; EP-A-0206624; and EP-A-0170386.

All these peracid compounds are usable in the bleach and/or detergent compositions of the invention and may be present in an amount of from 0.5 to 65% by weight of the total composition, preferably from 1-50%, particularly preferably from 1-25% by weight.

At these levels, the peracid bleach will be effective to give in the following test an increase in stain removal from tea-stained cotton of at least two reflectance units more than a similar product in which the peracid is replaced by sodium sulphate.

The tea-stained cotton is prepared as follows. A length of cotton sheeting is boiled for 1 hour in a concentrated infusion of tea. The cloth is removed, rinsed thoroughly, and dried at room temperature. The peracid is-tested in the following product:

Component (on anhydrous basis)	Parts by Weight
Linear alkyl (C12 to C18) benzene sulphonate	9
Nonionic 7EO	4
Sodium tripolyphosphate	33
Sodium alkaline silicate	6
Sodium carboxymethylcellulose	1
Magnesium silicate	1
Ethylene diaminetetraacetic acid	0.2
Water	10.8
Sodium sulphate	see below

The level of sodium sulphate is adjusted so that, after addition of the bleach, the parts by weight of the total formulation add up to 100.

4 gms of product is dissolved in 1 litre of 0°H water, and the pH of the solution is adjusted to equal the pKa of the peracid under test, using small quantities of sulphuric acid or sodium hydroxide solution. The test cloths are washed at 40°C for 30 mins in a Tergotometer operating at 75 r.p.m. After the wash the test cloths are rinsed and dried. The reflectances of the cloths at 460 nm are read before and after washing, using an Elrepho reflectometer fitted with an external filter to cut out incident radiation of less than about 400 nm. (Elrepho is a Trade Mark).

It is to be noted this test method defines the peracid environment in which the perfume compositions of the invention are usable. The increase of at least two reflectance units in the bleach activity will be dependent on the type of peracid used and its level in the formulation.

A laundry powder base with the formulation quoted was prepared.

50

5

10

15

20

25

30

35

40

	The peracid granules were about	
25		100.0
	•	
	social granutes	20.0
20	Peracid granules	10.8
	Water	15.0
	Sodium sulphate	0.2
15	EDTA	1.0
15	Magnesium silicate	1.0
	Sodium carboxymethylcellulose	
10	· Trade mark	6.0
	Alkaline sodium silicate	33.0
	Sodium tripolyphosphate	4.0
5	NONIONIC Surfactors (co.	9.0
	Component Linear alkyl (C12-C18) benzen sulphonate	Parts by wt
	_	

The peracid granules were obtained from Degussa GmbH of West Germany and had the composition:

Component	
Alpha omega-Diparentet	% wt
Alpha, omega-Diperoxydodecanedioic acid (DPDDA) Magnesium sulphate	12.0
Sodium sulphate	4.0
Binder	83.0
	1.0
	100.0

Laundry powder base (500 g) was dosed with perfume material (1.5 g) and then passed through a 20 mesh sieve. The remainder of the base powder (300 g) was added to the sieved base, placed in a Y-cone blender and blended for 10 minutes. After 10 minutes, DPDDA granules (200 g, 12% DPDDA content) were added and the whole was blended

Samples were taken from each port of the Y-cone blender and combined (10 g total) for initial analysis. The remainder was sampled into two sealed glass jars. The jar samples were stored at 0°C (control sample) and 37°C for 4 weeks. After storage, the perfume was extracted from the samples (solvent extraction with a suitable solvent) and analysed by gas-chromatography (gc), to determine the percentage of each perfume ingredient remaining relative to the control.

The analytical procedure was repeated ten times for a range of five perfume materials. Statistical analysis of the gc data gave an average percentage coefficient of variance of 1.25.

Results

30

*3*5

40

45

The test method described was applied to a number of perfume components and the peracid stability values (PSV) quoted as a percentage in Table I.

	Tabl	<u>le I</u>	PSV_(%)
5	i)	Saturated alcohols:	
		Tetrahydrogeraniol	81
		Decanol	100
10		Phenylethyl alcohol	92
		Phenylpropyl alcohol	100
15		o-tert-Butylcyclohexanol	100
		Dihydroterpineol	90
		di-Isobutylcarbinol	100
20		2,6-Dimethyl-2-heptanol	89
		Tetrahydrolinalol	88
25	ii)	Saturated esters:	PSV_(%)
		Tetrahydrolinalyl acetate	86
		MenthyI acetate	88
30		ortho-tert-Butylcyclohexyl acetate	100
		Dimethyl benzyl carbinyl acetate	99

5

	iii) Saturated aromatic ketones:	
5	Tonalid (6-acetyl-1,1,3,4,4,6-	PSV (%)
5	hexamethyltetrahydronaphthalene	
	obtainable from PFW of	
	Amersfoort, Netherlands)	
10	Benzophenone	74
	Methyl naphthyl ketone	98
	Traseolide (6-acetyl-1-isopropyl-	76
15	2,3,3,5-tetramethylindane from	
	Quest International of the Netherland	
	Celestolide (4-acetyl-6-tertbutyl-1,	ls) 58
20	1-dimethyl indane from IFF of Union	
_,	Beach, NJ, USA)	
		83
	iv) Saturated lactones:	PSV (%)
25	Hexadecanolide	92
	Sclareolide	73
	Lactoscatone (gamma-lactone of	, 3
30	1-hydroxy-3,10,10-trimethyl-bicyclo	
	[4,4,10] decane-3-carboxylic acid and	
	isomers from Dragoco of	
35	Holzminden, Germany)	82
		••
	v) Saturated nitriles:	PSV (%)
40	Frutonile (2-methyldecanonitrile	
	from Quest International of Ashford,	
	England)	98
	Dodecyl nitrile	100
45	Frescile (3-methyldodecanonitrile	
	rom Quest International)	100
50	vi) Saturated ethers:	PSV (%)
	Cedramber (cedryl methyl ether from	
	1FF)	81
55	Anther (Iso-amyl phenylethyl ether	

		from Quest International)	100
		Ph nylethyl methyl ether	93
5		•	
	vii)	Saturated acetals:	PSV_(%)
		Herboxane (2-butyl-4,4,6-trimethyl	
10		dioxan from Quest International)	69
		Indolal (indano [1,2-d]1,3-dioxane from	
		Dragoco)	100
15	viii	Saturated phenols:	PSV (%)
	·	Carvacrol	84
20	ix)	Saturated hydrocarbons:	PSV_(%)
		Diphenyl methane	99
		para-Cymene	99
25			
	x)	Saturated aromatic nitromusks:	PSV_(%)
	•	Moskene (Musk cymene from Givaudan	
30		of Geneva, Switzerland)	96
	xi)	Saturated salicylates:	PSV_(%)
35		Hexyl salicylate	51
55		Amyl salicylate	34
		Isoamyl salicylate	10
		Benzyl salicylate	0
40			
	xii)	Saturated aldehydes:	PSV (%)
		Dodecanal	0
45		Lilial (3-/para-tert.butylphenyl)	_
		-2-methylpropanal from Givaudan)	0
			DCU (%)
50	xiii)Saturated formates:	PSV (%)
		Phenylethyl formate	0
		CP formate (cyclohexane-1-methanol-	0
55		alpha-3,3-trimethyl formate from IFF)	•

i[]

5	xiv) Saturated aliphatic ketones: Fleuramone (2n-heptylcyclopentanone	PSV (%)
	from IFF)	0
	Orivone (4-(1,1-dimethylpropyl)-	
10	cyclohexanone from IFF)	0
	<pre>xv) Unsaturated alcohols:</pre>	PSV (%)
15	Primary	F3V [8]
	9-Decenol-1	6
	Cinnamic alcohol	0
	Geraniol	0
20	Citronellol	0
	Secondary	0
	Amylvinyl carbinol	0
25	Tertiary	0
	alpha-Terpineol	0
	Linalol .	0
30		U
	xvi) Unsaturated esters:	PSV_(%)
	Florocyclene (hexahydro-4,	450
35	7-methanoinden-5-yl propionate from	
	Quest International)	0
	Linalyl acetate	0
	Terpinyl acetate	0
40	Jasmacyclene (hexahydro-4,	· ·
	7-methanoinden-5-yl acetate from	
	Quest International)	4
45	•	•
	xvii) Unsaturated ketones:	PSV (%)
	alpha-iso-Methylionone	0
50	Lixetone (acetylated cedarwood from	
	Quest International)	0
	alpha-Ionone	0

9

	xviii)	Unsaturated nitriles:	PSV (%)
5		Geranyl nitrile	0
		Palmanitrile (isomeric mixture of	
		bicyclic nitriles from Dragoco)	1
10	xix)	Unsaturated esters:	PSV (%)
		Pelargene (from Quest International)	0
15	xx)	Unsaturated phenols:	PSV_(1)
		Eugenol	12
20	xxi)	Unsaturated aldehydes:	PSV_(%)
		Hexylcinnamic aldehyde	5
		Amylcinnamic aldehyde	0
25		Triplal (mixture of 3,5-dimethyl-	
		3-cyclohexene-1-carboxaldehyde and	
		2,4-dimethyl-3-cyclohexene-1-carbox-	
30		aldehyde from IFF)	0
	xxii)	:Unsaturated epoxides:	PSV (%)
		Myroxide (cis/trans isomers	
35		of ocimene epoxide from Firmenich	
		of Geneva, Switzerland)	. 0
	Examples of	perfume compositions satisfying the requirements of the present inventi	on are given below.

40 Composition A

	Component	Class	Parts per thousand
45			
	decanol	(i)	50
	phenylpropyl alcohol	(i)	60
50	diphenylmethane	' (ix)	50
50	Herboxane	(vii)	100

5	<pre>dimethylbenzylcarbinyl p-tertbutylcyclohexyl</pre>	acetate(ii)	150
	acetate	(ii)	175
	dihydroterpineol	(i)	30
10	tetrahydrolinalol	(i)	150
	Cedramber	(vi)	40
	hexadecanolide	(iv)	50
	Anther	(vi)	35
15	phenylethyl alcohol	(i)	60
	Traseolide	(iii)	50
			~~~~~
20			1,000

# Composition B

25

	Component	Class	Parts per thousand
30	dodecyl nitrile diphenylmethane carvacrol Herboxane	(v) (ix) (viii) (vii)	5 10 5
35	phenylethyl alcohol dimethylbenzylcarbinyl acetate phenylpropyl alcohol Celestolide Traseolide Moskene	(i) (ii) (i) (vi) (iii)	75 350 80 50 20 175
40	decanol Anther tetrahydrolinalyl acetate p-tertbutylcyclohexyl acetate	(x) (i) (vi) (ii) (ii)	30 40 60 50 50
45			1,000

# Composition C

50

*5*5

Component	Class	Parte por the
phenylethyl alcohol	<del> </del>	Parts per thousand
decanol	(i)	300
tetrahydrolinalol	(i)	10
tetrahydrogeraniol	(i) 	50
p-tertbutylcyclohexyl acetate	(i)	3
Continue	(ii)	150

Continuation of the Table on the next page

(continued)

Component	Class	Parts per thousand
Traseolide	(iii)	200
hexadecanolide	(iv)	10
Cedramber	(vi)	10
Moskene	(x)	30
Herboxane	(vii)	62
Frescile	(v)	5
dihydroterpineol	(i)	20
phenylpropyl alcohol	(i)	150
		1,000

## Composition D

5

10

15

	Component	Class	Parts per thousand
20	phenylethyl alcohol	(i)	250
	phenylpropyl alcohol	(i)	100
	o-tert.butylcyclohexyl		
25	acetate	(ii)	30
	dimethylbenzylcarbinyl		
	acetate	(ii)	180
30	benzophenone	(iii)	10
	Tonalid	(iii)	. 60
	Galaxolide	(vi)	160
35	Celestolide	(vi)	10
35	Anther	(vi)	50
	Frutonile	(V)	5
40	methyl naphthyl ketone	(iii	.) 20
	phenylethyl methyl ether	(vi)	35
	tetrahydrolinalol	(i)	90
45			
			1,000

# Bleach and Detergent compositions:

Detergent compositions containing peracids would be applied mainly to the cleaning of fabrics but are also usable to clean other substrates, e.g. hard surfaces.

Builder and detergent active components are well characterised in the field of detergent technology. Examples of these components are listed hereafter and full descriptions of these and other examples of these components will be found in "Surface Active Agents" by Schwartz and Perry published by Interscience (1949) and Volume II by Schwartz, Perry and Berch published by Interscience (1958). Examples of detergent actives usable at a level of from 5-50% by

weight in the compositions, which may be built or unbuilt, of the invention are present in the general classes of anionic, nonionic amphoteric, betaine and cationic actives. Specific classes usable singly or in admixture are:

- a) alkylaryl sulphonates having an alkyl chain from C10 to C15.
- b) alkyl (C12 to C18) sulphonates, wherein the alkyl group is branched or linear;
- c) alkali metal salts of alkane sulphonates having an alkyl chain length of from C11 to C14, these actives can be prepared by the reaction of a bisulphite ion species with an olefin;
- d) alkene sulphonates having a chain length from C14 to C24;
- e) sulphates of alcohols having chain lengths from 12 to 15, including branched chain alcohols obtainable under
- f) alkali metal salts of C8 to C22 long chain fatty acids; and
- g) dialkali metal salts of sulphonated saturated fatty acids having a chain length from C12 to C20;
- h) fatty acid ester sulphonates having from 8 to 20 carbon atoms in the fatty acid chain; 20
  - i) nonionic detergent actives, for example polyoxyalkylene derivatives of alcohols, alkylamides and alkanolamides, polyoxyalkylene esters of acids, alkylene oxide block polymers (eg. PLURONIC), polyol esters, acyl alkanolamides and ethoxylated alcohols (C8 to C20) having a degree of ethoxylation between 2 and 20. PLURONIC is a trade-mark.

The builder may consist of sequestrant, precipitant or ion-exchange materials, or their mixtures. Specific examples are sodium tripolyphosphate or pyrophosphate, sodium nitrilotriacetate, sodium oxydiacetate, sodium citrate, sodium tartrate and sodium carboxymethyloxy succinate, polymeric carboxylic acid salts derived from one or more of acrylic acid, methacrylic acid, maleic anhydride, and glyoxylic acid, e.g. Builder U of Monsanto, sodium carbonate with or without an insoluble seed material such as calcium carbonate, e.g. calcite, sodium orthophosphate, sodium C16-22 alkyl or alkenyl succinates, sodium C14 to C22 soaps, sodium alpha-sulpho fatty acid salts, soluble silicates and partially soluble layered silicates, amorphous or crystalline alumino-silicates, e.g. zeolites X, Y and A, and mixtures of any of the above. These materials are normally present in an amount of 5 to 80%, preferably from 10 to 60% by weight.

For many applications, a foam controller is desirably present. Non-limiting examples of these are C20 to C24 fatty acids or their salts, alkylphosphates, ethylene distearamide, and hydrophobed mineral particles such as silanised silica, all optionally mixed with hydrocarbon oils, waxes or polydimethylsiloxanes. These may be incorporated in any suitable amount and manner known to the art, e.g. sprayed on to a finished powder either directly or as a dispersion in a liquid carrier, e.g. an ethoxylated alcohol, or sprayed on to a solid porous substrate to form an adjunct which is then added to

Stabilising agents for the peracid may also be present. The amount of such agents, when present, is normally small, e.g. from 0.05-10% by weight, preferably from 0.1-5% by weight. Non-limiting examples of these are ethylene diamine tetra-acetic acid, diethylene triamine penta-acetic acid, ethylene diamine tetra-(methylene phosphonic acid), diethylene triamine penta-(methylene phosphonic acid) and their alkali(ne earth) metal salts, dipicolinic acid or its salts, and mag-

Other bleaches may be present in addition to the peracid bleach, such as hydrogen peroxide sources e.g. sodium perborate monohydrate and tetrahydrate, optionally with a precursor such as TAED. A list of possible precursors is given

The composition may include one or more optical brightening agents, such as the diaminostilbene/cyanuric chloride types, e.g. Blankophor MBBH, distyrylbenzene types, e.g. Tinopal CBS and Tinopal BLS, or triazole types, e.g. Blankophor BHC and Tinopal RBS. A combination of Blankophor BHC and Tinopal BLS is preferred for cotton fabrics and Blankophor (ex Bayer) and Tinopal (ex Ciba-Geigy) are trade-marks.

Various polymeric materials are of value as powder structurants, antiredeposition and anti-soiling agents, and for fabric care. Examples of these are the polymers and copolymers of monomers such as acrylic acid, methacrylic acid, and maleic anhydride, polymers and copolymers of ethylene oxide and/or propylene oxide, cellulose ethers, sodium

Buffering or pH adjusting agents may also be present to achieve a desired acidity or alkalinity. These are normally inorganic salts and examples are sodium metaborate, borax, sodium carbonate or bicarbonate, trisodium orthophos-

13

10

5

15

25

40

50

45

phate, disodium hydrogen phosphate, monosodium dihydrogen phosphate, tetrasodium pyrophosphate, trisodium hydrogen pyrophosphate, disodium dihydrogen pyrophosphate, sodium bisulphate, alkaline sodium silicate and neutral sodium silicate. Suitable organic salts and acids may also be used, in addition to or alternative to the inorganic salts. It is desirable that solid buffering agents be used in solid formulations, e.g. powders, but liquid pH adjusting agents, e.g. sulphuric acid, are used in liquid, gel or semi-solid formulations.

A preferred optional ingredient is an enzyme or a mixture of enzymes, which may be proteases and/or lipases. Specific examples of proteases are Alcalase®, Savinase® and Esperase® (obtainable from Novo of Denmark), Maxatase® and Maxacal® (obtainable from Gist-Brocades of Netherlands), Kazusase® (obtainable from Showa-Denko of Japan), Optimase® (obtainable from Miles Kali-Chemie of Hanover, West Germany), and Superase® (obtainable from Pfizer of USA). Specific examples of lipases are fungal lipases obtained from Humicola Lanuginosa or Thermomyces Lanuginosa, and bacterial lipases which react positively with the antibody of the lipase from Chromobacter Viscosum.

The composition may also include materials which confer a soft feel to washed fabrics. These may be one or more of hereinafter described clays at formulation levels of 2-15%, organo-clays at levels of 1-10%, amines and/or cationics at levels of 1.5-10%, silicones at levels of 0.5-5% and cellulase at levels of 0.1-10%.

Suitable clays are phyllosilicate clays with a 2:1 layer structure, the silicate layer being either dioctahedrally or trioctahedrally co-ordinated, and include the species saponite, hectorite, beidellite, or montmorillonite. Such materials are classed as smectite minerals, the most commonly distributed form being the bentonite earths, the major component of which is montmorillonite.

Suitable organo-clays are as described above, with the proviso that the alkali(ne earth) metals or proton exchangeable cations are partially or totally replaced with organic cationic materials.

Suitable amines are primary, secondary, or tertiary mono- or di- C10-C26 alk(en)yl amines; the tertiary dialkylamines in which the third alkyl chain is a C1-C4 alkyl are preferred. Other suitable amines are described in EP-A-0023367 (Procter & Gamble) and are tertiary amines with two C10-C26 alk(en)yl chains with the third group a moiety of several possible structures.

Suitable cationics are water-soluble or insoluble quaternary ammonium compounds of general formula (R1R2 R3R4N)+ Y- wherein at least one but not more than two of R1 to R4 is an organic radical containing a group selected from C16-C22 alkyl, or alkylphenyl or alkybenzyl having to 16 carbon atoms in the alkyl chain, the remaining R groups being selected from hydrocarbyl groups having 1 to 4 carbon atoms, C2-C4 hydroxyalkyl groups, cyclic structures in which the nitrogen forms part of the ring, e.g. imidazolinium compounds, and wherein Y- is a compatible counterion giving electrical neutrality.

Suitable silicones are organofunctional polyalkyl siloxanes, e.g. as described in EP-A-0150867 (Procter & Gamble). Suitable cellulases are bacterial or fungal cellulases having a pH optimum between 5 and 11.5, e.g. as described in GB-A-2075028 (Novo), GB-A-2095275 (Kao Soap), or GB-A-2094826 (Kao Soap).

Cellulose ethers at a formulation level of 0.05-5% may be used as a deposition aid with 2-40% of an organic hydrophobic softening material such as a calcium soaps, amines, cationics and mixtures of these. Suitable cellulose ethers are nonionic substituted cellulose ethers with an HLB between 3.1 and 3.8, gel points of less than 58°C and contain substantially no hydroxyalkyl groups containing more than two carbon atoms.

Other ingredients, for example starch, colouring materials, corrosion inhibitors, opacifiers, germicides and fillers, e.g. sodium sulphate, talc, calcite are optionally present.

The detergent formulation may be granular, liquid, a solid bar, or a semi-solid, e.g. a gel or paste. It may be supplied in bulk, e.g. in a packet or bottle, or in unit dose form, e.g. sachets or tablets.

Gelled formulations containing the peracid as a solid suspension may-require a thickening agent. Suitable thickening agents may be organic or inorganic, and examples are Laponite® or smectite clays, colloidal silicas, natural starches, gums and mucilages, e.g. corn, rice, and wheat starches, gum agar, gum arabic, and carrageenan, modified natural polymers, e.g. starch esters, carboxylmethyl cellulose, cellulose ethers, and hydrolysed proteins) and synthetic polymers, e.g. polyacrylamides, polymers and copolymers of acrylic acid, methacrylic acid and maleic anhydride monomers. The level of thickener used depends on the level and type of salts present in the formulation, but the gel will normally have a viscosity of 200-100,000 centipoise, preferably 200-20,000 centipoise.

50

15

20

25

30

35

40

EP 0 299 561 B1

s	20 1.5
10	ULATIONS  6  7  7
15	10ER FORM 20 20 20 20 20 20 20 20 20 20
20	EXAMPLES OF POWDER FORMULATIONS ulation  III
25	form 111 4 4 6 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
30	H * in 7 23 7 6 11 20 20 20 20 20 20 20 20 20 20 20 20 20
35	Sulphonate
40	COMPONENT Linear Alkylbenzene Sulpho Nonionic 7 EO  STPP Zeolite 4A  NTA  Sodium carbonate  Polyacrylic acid Acrylate/maleate copolymer Alkaline Silicate Neutral Silicate DPDDA granules  (12% active content)
45	COMPONENT Linear Alkylbenz Nonionic 7 E0 STPP Zeolite 4A NTA Sodium carbonate Polyacrylic acid Acrylate/maleate Alkaline Silicate Neutral Silicate DPDDA granules (12% active content)
50	COMP Line Noni STPP Zeol: NTA Sodiu Sodiu Polya ACFY]

5											•
10		<b>⋝!</b>	i	11	-	0.2	ı	i	0.3	i	j   
15		>!	10	10	г	0.2	ı	ı	ı	0.3	ļ
20		≥!		21	н	0.2	ı	0.3	ı	i	up to 100
25	(CONT.)		4	14	ч	0.2	0.3	1	ı	1	!
30	의	⊫d	0	₹.	-	0.2	ı		0.3		i
35		II I		12						ı	
40						•					
45			bonate	late			osition A	osition B	osition C	osition D	yı.
50		NENT	Sodium bicarbona	Sodium sulphate			Perfume Composit	Perfume Composit	Perfume Composit	Perfume Composit	Water, Minors
55		COMPONENT	Sodiu	Sodiu	SCMC	EDTA	Perfu	Perf	Perf	Perfu	Water

The minor components include for example additional stabilisers, fluorescers, enzymes and foam control systems.

# **EXAMPLE OF LIQUID FORMULATION**

i	,	

10

15

Component	% in formulation VII
Linear alkylbenzene sulphonate Nonionic 7EO Sodium sulphate EDTA DPDDA (100% active ingredient)	7 3 7 0.5
Perfume Composition A Water, minors	0.2 to 100

One minor component is a pH adjusting agent to bring the pH into the range 2.5 to 6.5, more preferably 3.5 to 4.5.

# **EXAMPLES OF GEL FORMULATIONS**

20

		in formulation				
25	Component	VIII	IX	<u>X</u>		
25	DPDDA (190% active ingredient) Laponite $^{f R}$	15	10	15		
	Polyacrylic acid*	-	-	6		
30	Corn starch	-	1	-		
	Perfume Composition B	13 0.3	_	-		
35	Perfume Composition C	_	0.25	_		
	Perfume Composition D	-	-	0.25		
	Citric acid	0.3	-	0.3		
	KH2PO4 EDTA	-	1	-		
40	Water	0.2	0.2	0.5		
			to 100			

M.W. ca  $4 \times 10^6$ .

## Claims

50

- 1. A bleach composition comprising an organic peracid bleach and a perfume composition comprising perfume components which do not contain alkenyl or alkynyl groups and have a PSV (Peracid Stability Value) of at least 65%, selected from the following classes:
  - i) saturated alcohols
  - ii) saturated esters
  - iii) saturated aromatic ketones
  - iv) saturated lactones

Laponite is a Trademark of Laporte Industries Ltd.

- v) saturated nitriles
- vi) saturated ethers
- vii) saturated acetals
- viii) saturated phenols

5

15

30

35

40

45

- ix) saturated hydrocarbons and
- x) saturated aromatic nitromusks

the said perfume components constituting from 0.05 to 1% by weight of the bleach composition.

- 2. A bleach composition according to claim 1, characterised in that it comprises an effective amount of said organic peracid bleach and up to 10% by weight of said perfume composition.
  - 3. A bleach composition according to claim 1 or claim 2, characterised in that said perfume composition comprises at least 80% by weight of said defined perfume components.
  - A bleach composition according to any one of claims 1 to 3, characterised in that said perfume components have a PSV of at least 80%.
- A bleach composition according to any one of claims 1 to 4, characterised in that it further contains a detergent active material.
  - A bleach composition according to any one of claims 1 to 5, characterised in that the said organic peracid bleach is 1,12-diperoxy-dodecanedioic acid.
- 7. A bleach composition according to any one of claims 1 to 6, wherein perfume components constituting from 0.05 to 1% by weight of the bleach composition are selected from:
  - i) Saturated alcohols: Tetrahydrogeraniol Decanol Phenylethyl alcohol Phenylpropyl alcohol o-tert-Butylcy-clohexanol Dihydroterpineol di-Isobutylcarbinol 2,6-Dimethyl-2-heptanol Tetrahydrolinalol
  - ii) Saturated esters: Tetrahydrolinalyl acetate Methyl acetate ortho-tert-Butylcyclohexyl acetate Dimethyl benzyl carbinyl acetate
  - iii) Saturated aromatic ketones: 6-Acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene Benzophenone Methyl naphthyl ketone 6-Acetyl-1-isopropyl-2,3,3,5-tetramethylindane 4-Acetyl-6-tertbutyl-1,1-dimethyl indane
  - iv) Saturated lactones: Hexadecanolide Sclareolide gamma-Lactone of 1-hydroxy-3,10,10-trimethyl-bicyclo [4,4,10] decane-3-carboxylic acid
  - v.) Saturated nitriles: 2-Methyldecanonitrile Dodecyl nitrite 3-Methyldodecanonitrile
  - vi) Saturated ethers: Cedryl methyl ether Iso-amyl phenylethyl ether Phenylethyl methyl ether
  - vii) Saturated acetals: 2-Butyl-4,4,6-trimethyl dioxan Indano [1,2-d]1,3-dioxane
  - viii) Saturated phenols: Carvacrol
  - ix) Saturated hydrocarbons: Diphenyl methane para-Cymene
- 50 x) Saturated aromatic nitromusks: Musk cymene

## Patentansprüche

 Bleichmittelzusammensetzung, umfassend ein organisches Persäurebleichmittel und eine Parfümkomposition, umfassend Parfümbestandteile, die keine Alkenyl- oder Alkinylgruppen enthalten und einen PSV-Wert (Persäurestabilitätswert) von mindestens 65 % aufweisen, ausgewählt aus den folgenden Klassen:

i) gesättigten Alkoholen

ii) gesättigten Estern iii) gesättigten aromatischen Ketonen iv) gesättigten Lactonen 5 v) gesättigten Nitrilen vi) gesättigten Ethern vii) gesättigten Acetalen viii) gesättigten Phenolen ix) gesättigten Kohlenwasserstoffen und 10 x) gesättigtem aromatischem Nitromoschus, wobei die Parfümbestandteile 0,05 bis 1 Gew.-% der Bleichmittelzusammensetzung ausmachen. Bleichmittelzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie eine wirksame Menge des orga-15 nischen Persäurebleichmittels und bis zu 10 Gew.-% der Parfümkomposition umfaßt. Bleichmittelzusammensetzung nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß die Parfümkomposition mindestens 80 Gew.-% der definierten Parfümbestandteile umfaßt. 20 Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Parfümkomponenten einen PSV-Wert von mindestens 80 % aufweisen. Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie außerdem einen Waschmittelaktivstoff enthält. 25 Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das organische Persäurebleichmittel 1,12-Diperoxydodecandisäure ist. 7. Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 6, worin die Parfümbestandteile, 0,05 bis 1 Gew.-% der Bleichmittelzusammensetzung ausmachen, ausgewählt aus: 30 i) Gesättigten Alkoholen: Tetrahydrogeraniol Decanol Phenylethylalkohol Phenylpropylalkohol o-tert.-Butylcyclohexanol Dihydroterpineol Diisobutylcarbinol 2,6-Dimethyl-2-heptanol Tetrahydrolinalol ii) Gesättigten Estern: Essigsäuretetrahydrolinalylester Essigsäuremethylester Essigsäure-ortho-tert.-butyl-35 cyclohexylester Essigsäuredimethylbenzylcarbinylester iii) Gesättigten aromatischen Ketonen: 6-Acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalin Benzophenon Methylnaphthylketon 6-Acetyl-1-isopropyl-2,3,3,5-tetramethylindan 4-Acetyl-6-tert.-butyl-1,1-dimethylindan 40 iv) Gesättigten Lactonen: Hexadecanolid Sclareolid γ-Lacton von 1-Hydroxy-3,10,10-trimethylbicyclo-[4,4,10] decan-3-carbonsäure v) Gesättigten Nitrilen: 2-Methyldecannitril Dodecylnitril 3-Methyldodecannitril 45 vi) Gesättigten Ethern: Cedrylmethylether Isoamylphenylether Phenylmethylether vii) Gesättigten Acetalen: 2-Butyl-4,4,6-trimethyldioxan Indano[1,2-d]1,3-dioxan 50 viii) Gesättigten Phenolen: Carvacrol ix) Gesättigten Kohlenwasserstoffen: Diphenylmethan p-Cymen x) Gesättigtem aromatischem Nitromoschus: Moschuscymen 55

## Revendications

5

10

15

25

40

45

50

55

- 1. Une composition de blanchiment comprenant un agent de blanchiment peracide organique et une composition de parfum comprenant des composants de parfum qui ne contiennent pas de groupes alkényle ni alkynyle et présentent une PSV (valeur de stabilité au peracide) au moins égale à 65 %, sélectionnés parmi les classes suivantes :
  - i) alcools saturés
  - ii) esters saturés
  - iii) cétones aromatiques saturées
  - iv) lactones saturées
  - v) nitriles saturés
  - vi) éthers saturés
  - vii) acétals saturés
  - viii) phénols saturés
  - ix) hydrocarbures saturés et
  - x) nitromuscs aromatiques saturés

lesdits composants de parfum constituant 0,05 à 1% en masse de la composition de blanchiment.

- 20 2. Une composition de blanchiment selon la Revendication 1, caractérisée en ce qu'elle comprend une quantité efficace dudit agent de blanchiment peracide organique et jusqu'à 10 % en masse de ladite composition de parfum
  - 3. Une composition selon la Revendication 1 ou la Revendication 2, caractérisée en ce que ladite composition de parfum comprend au moins 80 % en masse desdits composants de parfum définis.
  - 4. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 3, caractérisée en ce que lesdits composants de parfum présentent une PSV au moins égale à 80 %.
- Une composition de blanchiment selon l'une quelconque des Revendications 1 à 4, caractérisée en ce qu'elle comprend en outre une matière détergente active.
  - 6. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 5, caractérisée en ce que ledit agent de blanchiment peracide organique est de l'acide 1,12-diperoxydodécanédioïque.
- 7. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 6, dans laquelle les composants de parfum constituant 0,05 à 1 % en masse de la composition de blanchiment sont sélectionnés parmi :
  - i) Alcools saturés : Tétrahydrogéraniol Décanol Alcool de phényléthyle Alcool de phénylpropyle O-tert-butylcyclohéxanol Dihydroterpinéol Di-isobutylcarbinol 2,6-diméthyl-2-heptanol Tétrahydrolinalol
  - ii) Esters saturés : Acétate de tétrahydrolinalyle Acétate de méthyle Acétate d'ortho-tert-butylcyclohexyle Acétate de diméthylbenzylcarbinyle
  - iii) Cétones aromatiques saturées : 6-acétyl-1,1,3,4,4,6-hexaméthyltétrahydronaphtalène Benzophénone Méthylnaphtylcétone 6-acétyl-1-isopropyl-2,3,3,5-tétraméthylindane 4-acétyl-6-tertbutyl-1,1-diméthylindane
  - iv) Lactones saturées: Hexadécanolide Sclaréolide Gammalactone d'acide 1-hydroxy-3,10,10-triméthyl-bicy-clo [4,4,10]décane-3-carboxylique
  - v) Nitriles saturés : 2-méthyldécanonitrile Nitrile de dodécyle 3-méthyldodécanonitrile
  - vi) Ethers saturés: Cédrylméthyléther Iso-amylphényléthyléther Phényléthylméthyléther
  - vii) Acétals saturés : 2-butyl-4,4,6-triméthyldioxane Indano[1,2-d]1,3-dioxane
  - viii) Phénols saturé : Carvacrol
  - ix) Hydrocarbures saturés : Diphénylméthane Para-cymène

x) Nitromuscs aromatiques saturés : Cymène de musc

5